

Modeling Volatilization of Trichloroethylene from a Domestic Shower Spray: The Role of Drop-Size Distribution

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The factors affecting the volatilization of trichloroethylene from a shower spray were assessed and modeled as a function of the distribution of drop sizes. For the 10 L/min shower-water flow system, the measured drop sizes were smaller and initial velocities greater than those for the 5 L/min system. Log-probit plots indicate a bimodal distribution of drop sizes for each flow rate. Three models for internal mass transfer from drops were assessed to determine which best predicted shower emissions. A penetration theory model applied to oscillating drops, an eddy diffusion model, and a model for mass transfer restricted to a thin liquid film surrounding the drops was compared to data on volatilization from drops collected at different heights in the shower spray. The former two models fit the data. It was also observed that volatilization from water at the bottom of the shower was substantial.

Introduction

The release of volatile organic chemicals (VOCs) from a shower spray is controlled by the interfacial area of contact between the drops and air, drop velocity and residence time, and the mode of mass transfer from the drops to the air (e.g., eddy diffusion, molecular diffusion). All of these factors are a function of drop size. It follows then that knowledge of the drop-size distribution for a shower spray would aid in modeling the volatilization of VOCs from that spray. Using a model shower system, Andelman et al. (1) showed that the shower spray is one of two major sources of chemical emissions, the pool of water around the shower drain being the other. This experimental result emphasizes the need for a better understanding of the hydrodynamic regimes in the shower system, including drop sizes, which affect the volatilization process.

In the present study the drop sizes and velocities are determined experimentally for a standard-size shower head. This information is used, along with three models for internal mass-transfer constants for the rates of volatilization from the surfaces of water drops, to predict the emission of trichloroethylene (TCE) from the shower spray. These modeled results are then compared to those obtained from experiments measuring the volatilization of TCE from drops collected at different heights in the shower spray in an effort to determine which model(s) best predict volatilization of TCE from the experimental, full-size shower system.

Mass-Transfer Models for Volatilization from Drops

Three mass-transfer, volatilization models have been chosen for comparison to experimental results obtained in this work. They include penetration theory applied to oscillating drops (2), eddy diffusion from drops (3), and a model where all the mass transfer is restricted to a thin liquid film surrounding the drop (4). The last two models

depend on the drop velocity, whereas the first does not. These three models were chosen because others have studied their application using a spray-like system (5), they cover a range of mass-transfer mechanisms, and they give predictions in the mathematically convenient form of a mass-transfer constant.

Model 1: Angelo et al. (2). The penetration theory for mass transfer is generalized to oscillating drops. These drops experience sinusoidal oblate/prolate oscillations that result in the stretching and shrinking of their surface area. It is thought that drops undergo a violent internal mixing once a cycle. The liquid-phase controlled, mass-transfer constant for a single drop is

$$k_L = (2/\pi^{0.5})[\omega D_L(1 + \epsilon + 0.375\epsilon^2)]^{0.5} \quad (1)$$

where ω (1/s) is the frequency of oscillation given by Lamb's equation:

$$\omega = \frac{(8\sigma/3\pi m)^{0.5}}{2} \quad (2)$$

where σ (dyn/cm) is the surface tension of water and m (mg) the mass of the drop, D_L (cm²/s) is the diffusivity in water of the contaminant, and ϵ is the amplitude of oscillation. Still photos of the shower spray showed circular drops being emitted from the nozzle. This implies that any drop oscillation was quickly dampened, and therefore, ϵ was chosen to be zero.

Model 2: Handlos and Baron (3). The liquid-phase controlled, mass-transfer constant for a liquid drop moving through a fluid medium is given by

$$k_L = \frac{0.00375V}{1 + (\mu_d/\mu)} \quad (3)$$

where V (cm/s) is the drop velocity, μ_d (P) is the viscosity of water, and μ (P) is the viscosity of air (in this case). This equation is based on the assumption that all the mass transferred from the dispersed phase of the drop to the continuous phase is by eddy diffusion. The eddy diffusion transfer process involves motion from the bulk of the drop to the drop's surface. Subsequent volatilization mass transfer by molecular diffusion across the drop's surface is assumed to occur instantaneously, since the film thickness is assumed to be zero.

Model 3: Ruckenstein (4). This model assumes a well-mixed drop interior, with all the resistance to mass transfer occurring within a thin film of liquid around the outside of the drop. The continuous phase flows around the outside of the drop as it falls, causing the drop's internal mixing. This mixing is assumed to bring continuously fresh phases from the bulk water of the drop to its surface. The diffusion at the drop's surface is considered rapid but incomplete. The equation for the mass-transfer constant is

$$k_L = (2/\pi^{0.5})[V(D_L/d)]^{0.5} \quad (4)$$

where d (cm) is the drop diameter.

Modeling Spray Volatilization. The following is an application of the dual-resistance theory to describe the

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volatilization process for the shower spray. A comprehensive review of the dual-resistance theory has been presented by Haney (6).

A mass-balance expression may be written for volatilization from a single, spherical drop as

$$dC_L/dt = -K_{L_i}(6/d)(C_L - C_g/H) \quad (5)$$

where K_{L_i} (cm/s) is the liquid-phase controlled, mass-transfer constant for a chemical volatilizing from the drop; C_L is the aqueous-phase bulk liquid concentration of volatilizing chemical (mg/m³); C_g is its gas-phase concentration (mg/m³); and H is the dimensionless Henry's constant (the ratio of the gas-phase concentration for volatilized chemical divided by its aqueous phase concentration at equilibrium). Assuming the bulk liquid interior of the drop remains well-mixed, integration of eq 5 during the residence time in air of the drop yields

$$(C_L - C_g/H)/(C_{L_0} - C_g/H) = \exp[-K_{L_i}(6/d)t_d] \quad (6)$$

where C_{L_0} (mg/m³) is the feedwater concentration and C_L (mg/m³) is the concentration in the drop at the end of its residence time in air, t_d (s). Equation 6 thus expresses the concentration of chemical remaining in a single drop as a function of its residence time in air, feedwater concentration, and air concentration in the shower. It is assumed that the latter, C_g , remains constant during the short residence time in air (~0.5 s). The concentration of chemical remaining in the spray, as a function of air and water-phase concentrations and the residence time of the spray in the air, can be found by summing all the volume-weighted contributions of each drop size in intervals designated by d_i , from $i = 1$ to $i = n$, where n represents the total number of drop sizes in the spray

$$(C_L - C_g/H)/(C_{L_0} - C_g/H) = \sum_{i=1}^n \lambda_i \exp[-K_{L_i}(6/d_i)t_d] \quad (7)$$

where λ_i is the fractional volume for drop size i and K_{L_i} (cm/s) is the mass-transfer constant for that drop size. It should be pointed out that the assumption of spherical drops need not have been made to arrive at the final form of eq 7, although the specific factor $6/d_i$ is based on a spherical drop shape.

The fraction of chemical volatilized from the spray, f_v , is

$$f_v = 1 - C_L/C_{L_0} \quad (8)$$

Combining eqs 7 and 8, one obtains

$$f_v = [1 - C_g/H C_{L_0}][1 - \sum_{i=1}^n \lambda_i \exp(-K_{L_i}(6/d_i)t_d)] \quad (9)$$

This equation will be used to predict volatilization rates as a function of drop residence time, experimentally-determined drop-size distributions, and K_{L_i} values obtained from volatilization models. These calculated rates will then be compared to those determined experimentally to assess the accuracy of the models.

Experimental Section

Drop-Size Distributions in the Shower Spray. The measurement of the shower spray drop sizes was accomplished using the fact that horizontally-moving drops have different stopping distances which vary with drop size. Stopping distance is that which a particle, with some initial velocity, will travel through the air in a horizontal direction (for a discussion of stopping distance see ref 7). Velocities of the drops in the shower spray were measured using a

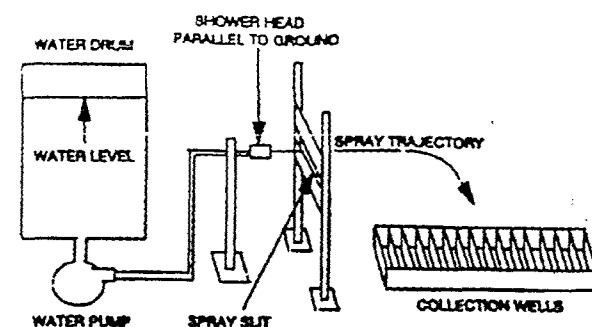


Figure 1. Schematic of drop-sizing apparatus.

video cassette recording system. Since both drop diameters and velocities were measured for the distribution of drops in the shower spray, their Reynolds numbers could be calculated. The Reynolds number is the ratio of inertia to viscous drag force a particle experiences as it moves through its trajectory in air. Smaller drops will have smaller Reynolds numbers and correspondingly shorter stopping distances because of high viscous air resistance. Larger drops, with the same initial velocity, have higher Reynolds numbers and experience more of an inertial resistance to motion. These larger drops will, therefore, have longer stopping distances. This concept of sizing drops on the basis of their different velocities has been used for rain drops (8).

Average velocity for the drops at 5 L/min was estimated to be 343 cm/s, and at 10 L/min 507 cm/s. These estimates were made from a video tape taken of the shower at 30 frames per second (the shower drop height was 183 cm). The leading edge of the spray was tracked and the distance fallen measured frame by frame by replay on a television screen. A tape measure stretched from the top to the bottom of the shower provided the markings for distance fallen. The drops were observed to move together in a plume and were therefore assumed to have the same average velocity.

The experimental setup for sizing the drops in the spray is shown in Figure 1. The shower head was mounted in a horizontal position so that the shower spray flowed parallel to the ground. Water was pumped to the shower head, from a 208-L polyethylene drum, using a Gelber positive displacement pump (Model HP 75-150B). The shower spray approximates a solid cone in cross section. Representative sampling of this cone was taken by passing the spray through a slit 0.8 cm high and as long as the width of the spray cone. A small gutter on the top side of the slit caught water not passing through the slit and drained it away, thus preventing the formation of interfering drops. The spray which passed through the slit was caught by trays with plastic walls. Each well was 5.5 cm deep, 5.5 cm wide, and 21.5 cm long. The entire apparatus was shielded on all sides from any cross breezes by plastic sheeting. The shower head was operated at a low flow of 5 L/min and a high flow of 10 L/min.

Calibration of the collection wells was done by placing glass plates (23 cm × 33 cm) covered with soot on top of each well. The shower spray was started with the slit initially covered. The slit was then uncovered for 1-2 s to allow drops to footprint the glass plates. These footprints gave true drop diameters (i.e., clear circles appeared on the sooted plates where the drops landed). After footprinting, the glass plates were covered with white paper towel to prevent smearing of the footprints. Each plate was placed on a lightbox, covered side down. For each well at least 100 drop diameters were measured using a mag-

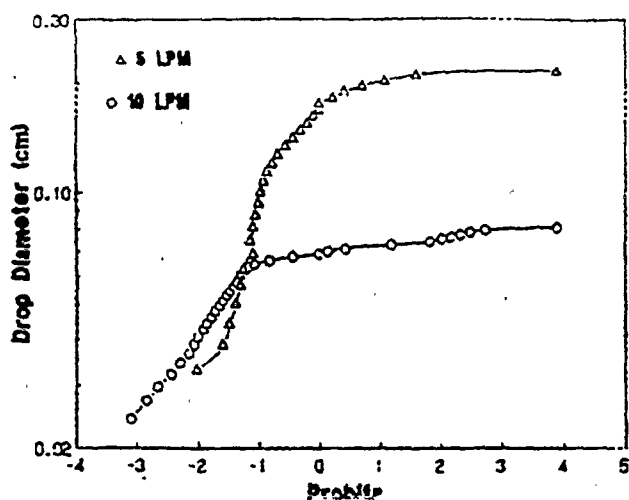


Figure 2. Drop-size distributions for flows of 5 and 10 L/min.

nifier with reticle (Finescale comparator stock pocket model). Twenty-nine wells were used for the drop sizing at 5 L/min and 36 at 10 L/min.

The distributions of drop sizes were obtained by allowing the shower to run long enough to fill the collection wells with a measurable volume of water. Splashing from well to well was not a problem. The volume in each well was measured by pouring the water out a hole, drilled in the bottom of the well, into a graduated cylinder. During filling, the holes were kept capped. The drop-size distributions for the shower operated at both 5 and 10 L/min are shown in Figure 2. Each of these distributions represents the average of two replicate experiments. Each drop diameter corresponds to the mean for the given well. The maximum standard deviation for these mean diameters was found to be 2%, although it was typically less.

Volatilization as a Function of Shower-Drop Residence Time. The TCE-spiked shower spray, operated in a vertical mode, was sampled at different heights using a movable trapping device in an enclosed full-size shower chamber. The aqueous TCE was injected into the shower from a closed polyethylene drum, and its concentration was measured from samples taken just prior to the shower head. Similarly, the spray samples collected at various heights were also analyzed for the unvolatilized TCE content. This sampling device and its component parts are shown schematically in Figure 3. The spray was sampled by moving the trap to a fixed height within the spray. The trap was allowed to purge for a sufficient length of time (three trap volumes) to ensure that the sample taken showed no bias from a previous sample.

Samples were collected at the end of the Teflon tubing leading from the trap with a 40-mL glass syringe. Typically 15-mL water samples were collected and analyzed using a microextraction technique (9-11). This involved injecting the sampled water into a miniert reactiflask (Pierce Chemical Co.) and extracting the TCE with pesticide-grade pentane (Pierce Chemical Co.), followed by analysis using a gas chromatograph equipped with an electron capture detector (Hewlett-Packard Model 5890A). Feedwater samples were also taken from a Teflon tee in the line supplying the shower head. Again, 15-mL samples were taken using a 40-mL glass syringe, and analysis of the aqueous TCE concentration was done in the same way as for the shower-spray samples.

During each experiment the shower chamber was operated in an enclosed mode so that all parameters could be controlled and monitored in a precise manner. The air

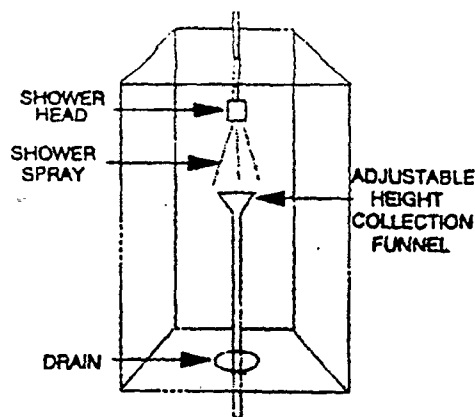


Figure 3. Schematic of movable shower spray trapping device.

concentration of TCE was monitored in real time using a Miran 1A, an infrared air monitoring device (Foxboro Co.). Feedwater concentration of TCE was kept constant in the water delivery system. Water flow rate was fixed at either 5 or 10 L/min. Water and air temperatures were measured in real time. The air-exchange rate of the shower chamber was also controlled (11).

Results and Discussion

The measured distributions of drop sizes are shown in Figure 2 for the 5 and 10 L/min water flow rate experiments. They can be shown to fit bimodal log-normal distributions. Their median drop sizes are quite different, indicating that water flow rate should affect volatilization in that the models discussed earlier show a dependency on drop size. The measured average percent volatilization of TCE was 67% and 59% at 5 and 10 L/min, respectively. However, the air-exchange rates in the volatilization chambers for these two experiments were also different at 3.5 and 1.3 air exchanges per hour (ACH), respectively. The air-exchange rate can affect the inhibition of the volatilization rate since it affects C_a . As the latter increases and the Henry's law equilibrium is approached, as indicated by eq 5, there is a decrease in the driving force ($C_L - C_a/H$) for mass transfer of the VOC from the shower water to the air. Thus, the differences in the percent volatilization in these two experiments may not be due entirely to differences in drop-size distributions. However, McKone and Knezovich (12) did not find a statistically significant difference in transfer efficiency for TCE during a 20-min shower period during which the air concentration of TCE would have increased with time. Also, for both hot and cold showers they found that on the average the transfer efficiency was about 60%, similar to the values we report here.

The results for the relationship between fractional volatilization and drop-residence time for two typical spray-sampling experiments are shown in Figures 4 and 5. The air and water temperatures of these experiments are shown there, as are the shower-water inlet concentrations of TCE, 480 and 780 $\mu\text{g/L}$, respectively. The TCE air concentrations during the drop-residence time, also shown in these figures, were substantially different for the two water flows. The experimental data are represented by the open circles, which are connected by solid lines and include error bars corresponding to 1 SD of imprecision associated with the TCE analyses. The dashed lines represent the modeled predictions. These latter curves were calculated for models 1, 2, and 3 using the k_L values determined from eq 1, 3, and 4, respectively, in combination with the drop-size distributions shown in Figure 2, and the

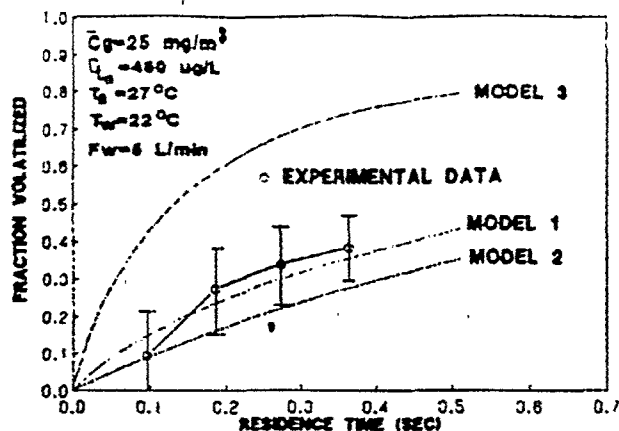


Figure 4. Concentration of TCE in shower spray as a function of residence time for experiment at 5 L/min with 1 SD experimental ranges.

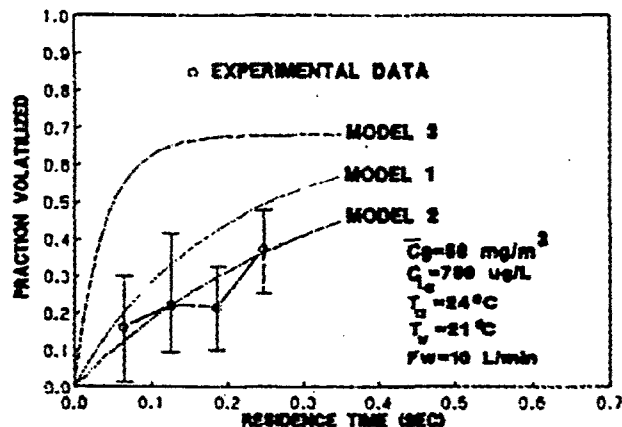


Figure 5. Concentration of TCE in shower spray as a function of residence time for experiment at 10 L/min with 1 SD experimental ranges.

application of eq 9. The raw data for both of these room-temperature shower experiments show that about 40% of the TCE in the feedwater volatilized from the spray before it reached the pool of water at the base of the shower chamber. The spray sample closest to the pool was taken 58 cm above it; since the total drop height was 183 cm, the fraction of TCE volatilized from the shower spray is likely to have been greater than 40%. As noted previously, the total percent volatilization for the experiment at 5 L/min was 67% and at 10 L/min was 59%. Since no water was observed running down the sides of the shower chamber during the shower experiments, the remaining fraction of chemical volatilized would have to have emanated from the pool.

The general trend for the curves in Figures 4 and 5 shows a rise in the fraction of TCE volatilized from the shower spray with increased residence time in air, as predicted by the three models for internal mass transfer from drops. Model 3 (velocity dependent) overpredicts in each case to a large extent. Model 2, the other velocity-dependent model, comes closer to matching the data, as does model 1. The latter is the surface-stretch model where penetration theory has been applied to volatilizing drops. Model 1 is particularly convenient to use because it predicts mass-transfer constants for all the drops in the spray-like system that do not change with velocity.

Models 1 and 2 predict that the 5 L/min drop-size distribution would result in substantially lower transfer efficiencies at each residence time compared to that for

10 L/min. The experimental differences for these two water-flow rates, although qualitatively consistent with these predictions, are not as great as the models predict.

The error bars shown in the experimental data in Figures 4 and 5 encompass a range of one relative standard deviation (rad) based on reproducibility of the measured inlet water concentration C_L and outlet water concentration C_g . In addition there is some imprecision in the model curves, since they utilize the experimental drop-size distributions and velocity measurements. However, only the latter were found to contribute significantly to the imprecision of the model curves. The mean velocities used in models 2 and 3 were 343 ± 27 (± 1 rad) for 5 L/min and 507 ± 61 for 10 L/min. When the velocity-dependent models 2 and 3 were run using extreme values of velocity (mean ± 1 rad), some range in fractional volatilization resulted, although it is small and is not shown in the plots. A more pronounced effect was seen for predictions at 5 L/min than at 10 L/min. The high velocity used in modeling 5 L/min brought model 2 closer to model 1, and the low velocity was still within the error-bar range of the data. Model 3 remained far removed from the data. For example, the largest imprecision due to velocity was found for model 2 at 10 L/min at a residence time of about 0.35 s. In this case 1 rad of velocity led to a rad of about ± 0.06 for f_v . For the other models and the lower 5 L/min flow rate, the uncertainty in f_v was substantially less. In conclusion, the uncertainty in the experimental measurements of f_v at various residence times, as well as that in the three model curves, indicate that models 1 and 2 overlap with and are consistent with experimental data, while model 3 is not.

At the water temperature of these two experiments, 22°C , the dimensionless Henry's law constant for TCE is 0.33 (11). The maximum measured values for C_g/C_L in each experiment occur at the longest measured residence time where C_g is the smallest, since C_L remains constant in each of the plots shown in Figures 4 and 5. For 5 L/min this maximum C_g/C_L is 0.09, and for 10 L/min, 0.16. This indicates that the Henry's law equilibrium was not attained in either of these experiments at the maximum measured residence time. As residence time increases, so should f_v , as volatilization continues, and models 1 and 2 show this. In contrast, at 10 L/min model 3 predicts that volatilization would essentially cease after a residence time of about 0.2 s due to attainment of the Henry's law equilibrium, since f_v stops increasing beyond that point. This is a further indication that this model does not accurately predict volatilization in our system. In actual domestic shower systems, it is unlikely that TCE would approach equilibrium unless there is a very long shower period, very high water-flow rate, and very low air exchange.

Altwick and Lindhjem (5) assessed the applicability of these three models to a spray-like system. They concluded that velocity-dependent models for internal mass transfer from drops did not explain the experimental data well, because even though the drops accelerate over the course of their residence time in air, their mass-transfer constants remained unchanged. Thus, the nonvelocity-dependent model 1, which we find to be more convenient to use because the mass-transfer constants are independent of drop velocity, may also be more generally appropriate. They also found that all three models overpredicted the measured mass transfer of CO_2 into their spray-like system.

The results reported here indicate that if modeling of the volatilization from a shower system is to be realistic, one must consider contributions from different sources within the shower system, such as the shower spray and

pool of water around the shower drain. Also, the physical characteristics and hydrodynamics of the shower system, including water-flow rate, can affect the volatilization process through their impacts on drop-size distribution and drop-residence time. It can be concluded from this work that the mass transfer of VOCs from the shower spray should not be modeled simply as occurring from a mono-dispersed, spherical drop-size distribution.

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